ICP-MS DETERMINATIONS OF HEAVY METALS IN SURFACE WATERS FROM TRANSYLVANIA*

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This study proposed to investigate the quality of surface waters used as raw water source by Water Treatment Plants which provide drinking water for a large number of inhabitants. Studied area includes two districts from Transylvania, namely Cluj and Salaj. A wide number of metals were identified in all water samples; usually in most water samples the amounts of such toxic metals were between the ranges of few μg/l. Inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique used for elemental determinations; the Perkin Elmer Elan DRC(e) ICP-MS instrument was used to perform water samples analysis.

*Key words***:** surface water, ICP-MS, heavy metals.

1. INTRODUCTION

Environment is an essential element of human existence. It is a result of interference of natural elements – earth, air, water, climate, biosphere – with elements created by human activity [1]. All these interact with/and influence the existential conditions and the possibilities for future development of society. To protect the environment, mainly affected areas must be identified, assessed the degree of damage and determined the causes that have produced these imbalances. It is necessary to preserve the quality of the environment mainly throughout reducing negative effects of human activities. Potentially toxic metals resulting from anthropogenic activities cause severe disturbance of ecosystems [2, 3].

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Water pollution is a complex process that leads to changes in water composition, aquatic flora and fauna, and may result in a poor condition, water quality for economic and recreational use, being dangerous to human health [4–6]. Importance of trace metal concentrations evidence in natural waters and/or environment is growing for the pollution monitoring studies. Traces of metal ions have important roles in a wide spectrum of functions of life. Some of these toxic trace metal levels are high, such as poisoning by Fe, Pb, Ni affects the central nervous system. Heavy metals presence in nature usually is not dangerous for the environment because they are present only in very small quantities [7]. Heavy metals are pollutants in the environment only if it's present in large quantities (this fact is usually attributed to industrial activities).

Most of these compounds quantitative presence in surface waters are regulated by the Romanian Ministry of Environment – STAS 4706/88 (Table 1).

Table 1

Categories and technical requirements for surface water-quality streams in case of natural or landscaped, natural lakes and reservoirs [8]

Indicator	**Symbol**	**U.M.**	**Quality categories**		
			I	**II**	**III**
Physical indicator - pH		Unites pH	6.5-8.5		
Specific chemical indicators					
Ag	Ag^{+2}	mg/dm^3	0.01	0.01	0.01
As	As	mg/dm^3	0.01	0.01	0.01
Ba	Ba^{+2}	mg/dm^3	1	1	1
Cd	Cd^{+2}	mg/dm^3	0.003	0.003	0.003
Co	Co^{+2}	mg/dm^3	1	1	1
Cu	Cu^{+2}	mg/dm^3	0.05	0.05	0.05
Hg	Hg^{+2}	mg/dm^3	0.001	0.001	0.001
Mo	Mo	mg/dm^3	0.05	0.05	0.05
Ni	Ni^{+2}	mg/dm^3	0.1	0.1	0.1
Pb	Pb^{+2}	mg/dm^3	0.05	0.05	0.05
Se	Se	mg/dm^3	0.01	0.01	0.01
Zn	Zn	mg/dm^3	0.03	0.03	0.03

2. EXPERIMENTAL

2.1. MATERIALS AND REAGENTS

This study proposes to investigate the quality of surface waters used for human consumption on an extended area in two counties in Transylvania. Samples were taken from areas adjacent to the accumulation of raw water from Cluj and Salaj. Water samples were collected in high density polyethylene containers previously washed in a solution of 10% nitric acid in an ultrasonic bath for 15 minutes, followed by repeated rinsing with bidistilate water and finally rinsing with ultrapure water (resistivity 18 $M\Omega cm^{-1}$). Until collection containers were kept in sealed polythylene bags. Water samples were stabilized with ultrapure nitric acid (0.5% HNO_3).

For accurated determination of concentrations of metals in waters, a quantitative method was used, therefore a multi-standard calibration method was applied: Perkin Elmer 10 mg/ml of twenty-nine metals (ICP-MS Standard, Matrix: 5% HNO_3, Perkin Elmer Life and Analytical Sciences), a standard of 10 mg/ml Hg (Mercury standard 5% HNO_3 matrix, Perkin Elmer), and multi-standard PerkinElmer 10 mg/ml rare-metal standard (Atomic Spectroscopy Standard, Matrix 5% HNO_3).

2.2. INSTRUMENT

All the determinations were done with inductively coupled plasma quadrupole mass spectrometry (ICP-Q-MS). ICP-MS is a relatively new method for determining multi-element analysis and ideal for water, since the vast majority of target compounds can be detected below 0.1 mg/l [9, 10].

Therefore a Perkin Elmer ELAN DRC (e) instrument was used with a Meinhart nebulizer and silica cyclonic spray chamber and continuous nebulization. The operating conditions are listed below: Nebulizer Gas flow rates: 0.95 l/min; Auxiliary Gas Flow: 1.2 l/min; Plasma Gas Flow: 15 l/min; Lens Voltage: 7.25 V; ICP RF Power: 1100 W; CeO/Ce = 0.031; Ba^{++}/Ba^{+} = 0.016.

3. RESULTS AND DISCUSSIONS

Table 2 presents the concentrations of metals that were determined in water samples taken from the following areas from Cluj County: Dam Gilău (sampling area 1), Somes Cald River (sampling area 2), Head Lake Gilău (sampling area 3), Somes Cald Lake (sampling area 4), Junction of Lakes Somes Cald/Somes Rece (sampling area 5), Somes Rece Lake (sampling area 6), Tarnita – a beach (sampling area 7), Tail Tarnița Lake-out of hydro (sampling area 8), Tail Tarnita Lake – to Belis (sampling area 9).

Table 2

Metal content in surface waters from Cluj-County

Sampling area	Metal concentrations [μg/l]										
	Al	**As**	**Pb**	**Cd**	**Ag**	**U**	**Zn**	**Mn**	**Ni**	**Co**	**V**
1	13.780	0.713	0.048	0.003	0.003	0.150	0.188	8.381	0.445	0.570	0.104
2	5.865	0.445	0.012	0.002	0.013	2.579	0.146	1.587	0.766	1.378	0.010
3	17.158	0.456	0.034	0.002	0.005	0.535	0.230	4.020	0.425	0.754	0.148

Table 2 (continued)

4	8.632	0.472	0.018	<LOD	0.003	0.124	0.133	3.354	0.285	0.625	0.108
5	9.807	0.479	0.017	0.001	0.003	0.131	0.139	2.036	0.294	0.562	0.107
6	8.167	0.491	0.017	0.001	0.003	0.126	0.144	4.293	0.295	0.532	0.067
7	14.471	0.432	0.023	0.002	0.003	0.120	0.268	5.871	0.331	0.632	0.128
8	16.727	0.555	0.032	0.001	0.002	0.127	0.175	8.398	0.325	0.543	0.157
9	5.044	0.241	0.014	0.002	0.003	0.162	0.288	5.071	0.346	0.509	0.102

Arsenic is widely distributed in the environment because of its natural and anthropogenic sources [11]. In surface and groundwater, arsenic is found dissolved in inorganic form (arsenite, arsenic) and organic form (acid-monimetilarsonic MMA-DMA dimetilarsinic acid). Inorganic arsenic is know to have high levels of toxicity, the allowable limits of As in natural mineral water (Commission Directives 2003/40/CE/ may 2003) and water for human consumption (Commission 98/83/CE/3 Directives. nov. 1998) was reduced to 10 mg/l total arsenic. Obtained levels in analyzed waters were below acceptable limits.

Lead is one of the most abundant heavy metals in nature. It is an essential nutrient but could be also toxic for humans [12]. Most important anthropogenic source of lead in the environment is combustion of gasoline with lead. In environmental, lead suffers lead changes and find that the Pb^{2+} ion or as insoluble lead compounds. Residence time in blood and soft tissues is one month, but in case of liver is 50 years [13]. Maximum permissible limit for lead in drinking water is 0.01 mg/l [14]. The values obtained in the analyzed waters are well below this value.

Aluminum is an essential nutrient for humans. Water analysis showed concentrations in the 5-20 mg/l.

Zinc is present in natural waters in concentrations lower than the sewer water, which comes from human activities related to galvanizing, zinc and copper alloys or other metals. Zinc ions are present in a concentration greater than 5 mg/l in water, which gives an astringent taste. Water could become cloudy, so is recommending that zinc concentration in water to be less than 5 mg/l. The values obtained for the waters are below this limit.

Accumulation of metal ions in surface water is important to be knownin order to classifying them for quality into several sections. Thus, in terms of metal content, raw water are situated in category I through STAS 4706/88. From sampling point area view, it could be concluded that: in the one-barrier sample was obtained Gilău concentration of pollutants like As, Cd, Mn, Pb; in second sampling Somes Cald River higher values of concentrations of U, Cu, Ni were obtained; highest concentration of Mn appears in Tail Tarnita Lake and Al in Zone 3 (the end of Gilău lake).

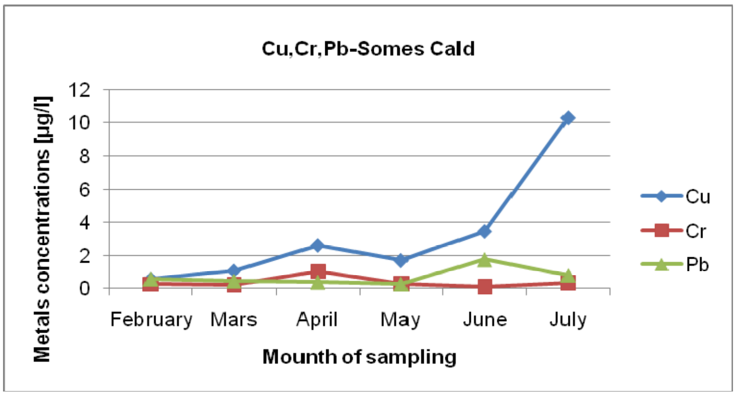

Fig. 1 – Concentrations of Cu, Cr, Pb in water from Somes Cald.

Selenium is recognized as an essential nutrient, it is present in the human body in an enzyme (glutathione peroxidase) that protects cells against oxidative threat [15]. Its recommended maximum concentration level in drinking water is 50 µg/l. For selenium determination, is shiwed an increased interest because of its dual role: essential nutrient at low concentrations and possible toxic effects at high concentrations. Narrow range of concentrations between the two opposing effects requires knowledge of accuracy and precision of selenium species in the environment. Toxicity and its nature depend on its chemical form. Their concentration in water has been under the method detection limits.

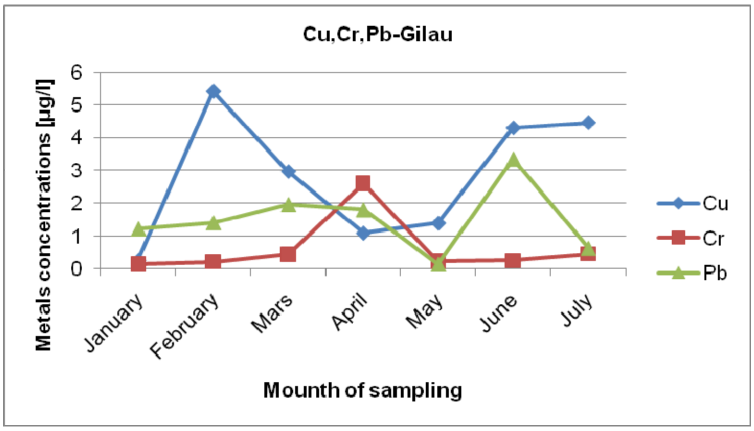

Fig. 2 – Concentrations of Cu, Cr, Pb in water from Gilau.

Chromium is another omnipresent element, not only because of its nature, but also due to its several anthropogenic sources, mainly coming from its large application in industrial fields.

Comparative characterization in terms of concentrations of Cr, Pb, in the water samples taken from raw water reservoirs Tarnita, Somes Cald and Somes Rece showed that the highest concentrations of Cu, Cr, Pb were in samples taken from Tarniţa in June and lower values in samples collected in January from the same location.

Copper could be present in water in ionic form or in complex organomineral. Copper, in particular, plays a dual role in the metabolism of photosynthetic organisms. It is both a micronutrient and a toxicant depending on the dose [16]. It is recommended that its level to not exceed the maximum permissible values for drinking water which is 1.0 mg/l. The highest concentrations of copper in samples collected from Somes Cald were obtained in July (up to 10 mg/l). Highest concentrations of Cr and Pb were obtained in samples taken from Somes Cald and Gilău in April (Cr), June (Pb) and the lowest concentrations of Cr, Pb, Cu in January (Figures 1, 2). However, the concentration values obtained for the four metals are below the accepted standard.

Water acidity increases the mobility and bio-availability of items that total dissolved solids concentration. Many of the metal ions increase their solubility in acidic and oxidizing conditions; in addition, metals are adsorbed on the surface of solids at low pH. In many cases high concentrations of heavy metals in water are associated with acidic and oxidizing conditions. In Table 3 are given the pH values in samples collected from the Tarnita, Somes Cald, Gilău in January-July. Values are normal (in the range 6.5-8.5, according to regulations).

Also were characterized water samples taken from different locations in Salaj County, North-Western Transylvania, like: Crasna, Şimleul Silvaniei (treated, filtered), Zalau (water-treatment plant entrance), Zalau (water-treatment plant output), Varsolt Lake, Hororatu Crasnei, Jibou (treated water, filtered). Varşolt Lake is located in the catchment Crasna; the main functions of accumulation are: water supply to city and town Zalau Şimleu-Silvaniei, mitigation of flood waves on the river Crasna; ensuring the flow of servitude downstream accumulation of 50 l/s.

Table 3

Physical-chemical surface waters from Cluj County

Time	Sampling area/ pH [unites pH]		
	Tarniţa	Someş Cald	Gilău
January	6	-	6
February	7.38	7.06	7.39
Mars	7.33	6.7	6.9
April	7.37	7.56	7.73
May	7.33	7.24	7.35
June	7.2	7.82	7.37
July	7.69	7.49	7.73

Most samples taken from the Salaj County present values which are relatively close to the measured concentrations of elements at different locations. A comparison of treated water samples (Şimleul Silvaniei Treatment water output station, Jibou) and waste water sample (water Treatment Zalau input station) or water samples originating from lakes (Crasna, Hororatu Crasnei, Varsolt) did not differ significantly in the concentrations of toxic metals or rare metals (Figure 3). Concentrations of toxic metals in water samples analyzed are below the limits imposed by regulations.

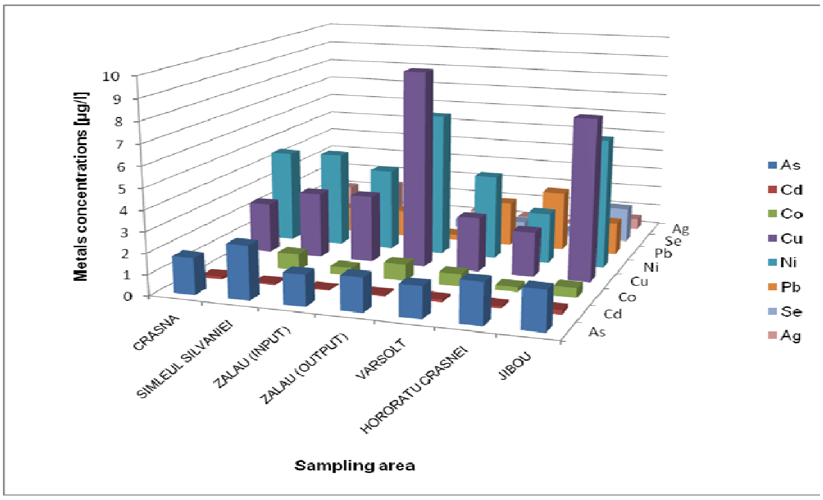

Fig. 3 – Heavy metal concentrations in waters from Salaj County.

The comparative characterization of water/water resulted from settling sediment stressed that accumulates large quantities of toxic metals (Table 4).

Mass spectrometry with inductively coupled plasma offers the possibility of measuring rare earth with great accuracy, which can not be achieved by another method [17]. The usefulness of determining rare earth comes from the fact that the results can be used to create an overview of the sample and thus the results can be used in determining the origin of the sample in question or identifying sources of pollution. Determination of rare earth can be used in hydro-geochemical studies because of their potential to provide information about the interactions between water and rocks and in some cases to determine groundwater flow. For surface water samples with a lower degree of pollution, the concentration of rare-metals is near or even below the limit of quantification.

Characterization of water in terms of rare metals and characterization of water resulting from decantation sediment revealed, as illustrated in Figure 4 that sediments accumulate rare metals. Sure, water and sediment concentrations are very low, but there is a slight increase in their sediment.

Table 4

Heavy metal concentrations in water/water from sediment

Sampling area	Sample	Metals concentrations [µg/l]				
		As	Cd	Pb	Co	U
Beliş	water	0.245	0.001	0.011	0.079	0.039
	water from sediment	0.265	0.018	0.122	0.079	0.054
Tarniţa	water	0.332	0.006	0.001	0.051	0.075
	water from sediment	0.346	0.010	0.019	0.073	0.107
Someş Rece	water	0.430	0.005	0.003	0.046	0.800
	water from sediment	0.629	0.007	0.002	0.100	1.233

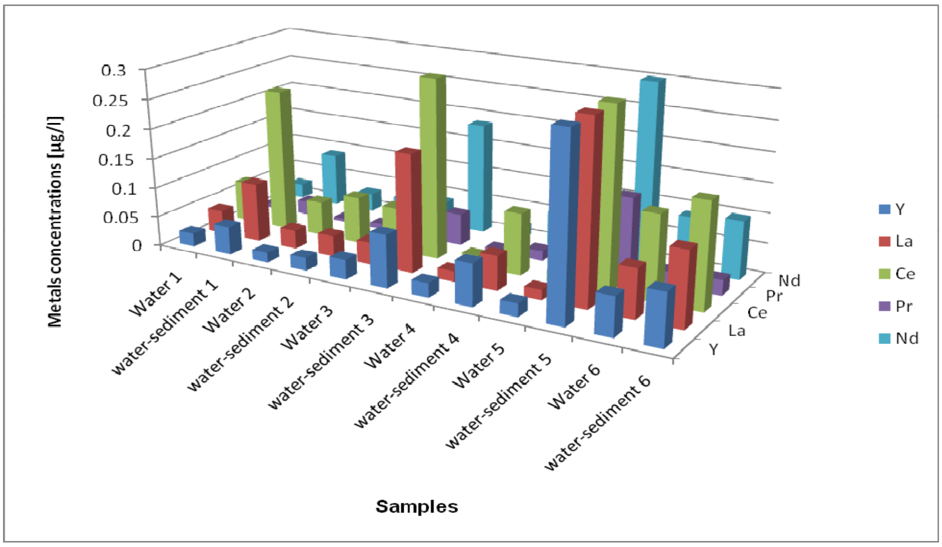

Fig. 4 – Comparative dates for rare metals concentration in water/water from sediments.

4. CONCLUSIONS

ICP-MS method is available and adequate to identify and quantify metals present in natural and drinking waters at trace levels, which are of particular relevance for toxicity control regions, may have been contaminated by toxic metals.

Waters from various areas surrounding the accumulation of raw water from Cluj and Salaj were characterized. Was quantitatively determined heavy metal concentrations in 0.001-25 mg/l. Measurements made on samples taken from different areas at different months in Cluj County highlighted low levels of toxic metals As, Cd, U, Pb, Co under permissible limits, concentrations of Al contained in 5-20 mg/l Zn concentrations below the limit allowed by regulations. Mn concentration was observed in the area of Lake Tail Tarnita, in the end of the lake

Gilău Al, Cu, Ni in samples taken from the Somes Cald. Concentrations of toxic metals in water samples are analyzed in the Salaj County of limits imposed by regulations. All water samples were characterized by Se concentrations below method detection limits (<0.001μg/l). For most samples taken from the Salaj County, measured concentrations of it are relatively close to another area, concentrations of toxic metals are below the limits imposed by regulations.

There is a variation of concentrations of heavy metals depending on the season, certain times of year. Characterization in terms of concentrations of Cr, Pb, Cu of water samples taken from raw water reservoirs Tarnita, Somes Cald, Somes Rece early the year showed that the highest concentrations of these elements (in Tarnița area) have been reported in samples taken in June and lowest in January. This could probably be explained by the fact that the pollution originates in effect driving the heavy metals to storm water to "wash" adjacent area before reaching the lake. In the summer months is normal that the effect is more pronounced than in the cold winter months, when the ground is frozen, and thus less exposed to erosion.

Determination of rare earths in various types of environmental samples is very important because it can use to create a fingerprint of the sample and thus the results can be used in determining the origin of the sample in question and to identify sources of pollution. For surface water samples characterized by a lower degree of pollution, the concentration of rare metals is close to or even below the limit of quantification, the concentrations were within the range 0.001-0.5 μg/l (except Sc 0.5–5 μg/l). Characterization in terms of concentrations of rare metals, comparative water/waters resulting from sediment decantation, revealed that sediments accumulate rare metals (water and sediment concentrations are very low, but there is a slight increase in their sediment).

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